

# Synthesis and Characterization of a New Type of Sulfonated Poly(ether ether ketone)s for Proton Exchange Membranes

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**ABSTRACT:** A novel series of sulfonated poly(ether ether ketone)s (SPEEKs) were prepared by aromatic nucleophilic polycondensation with different ratios of 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene to 1,3-bis(4-fluorobenzoyl)benzene. <sup>1</sup>H-NMR spectroscopy was used to confirm the degrees of sulfonation (DS) of the polymers. Thermal stabilities of the SPEEKs in acid form were characterized by thermogravimetric analysis (TGA), which showed that SPEEKs were excellently thermally stable at high temperatures. SPEEK polymers

can be easily cast into tough membranes. Both of proton conductivity and methanol diffusion coefficient have been tested in this article. Other properties of the SPEEK membranes were investigated in detail. The results show that the SPEEK membranes are promising in proton exchange membrane fuel cells (PEMFCs) application. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1515–1523, 2010

**Key words:** polyelectrolytes; membranes; fuel cells

## INTRODUCTION

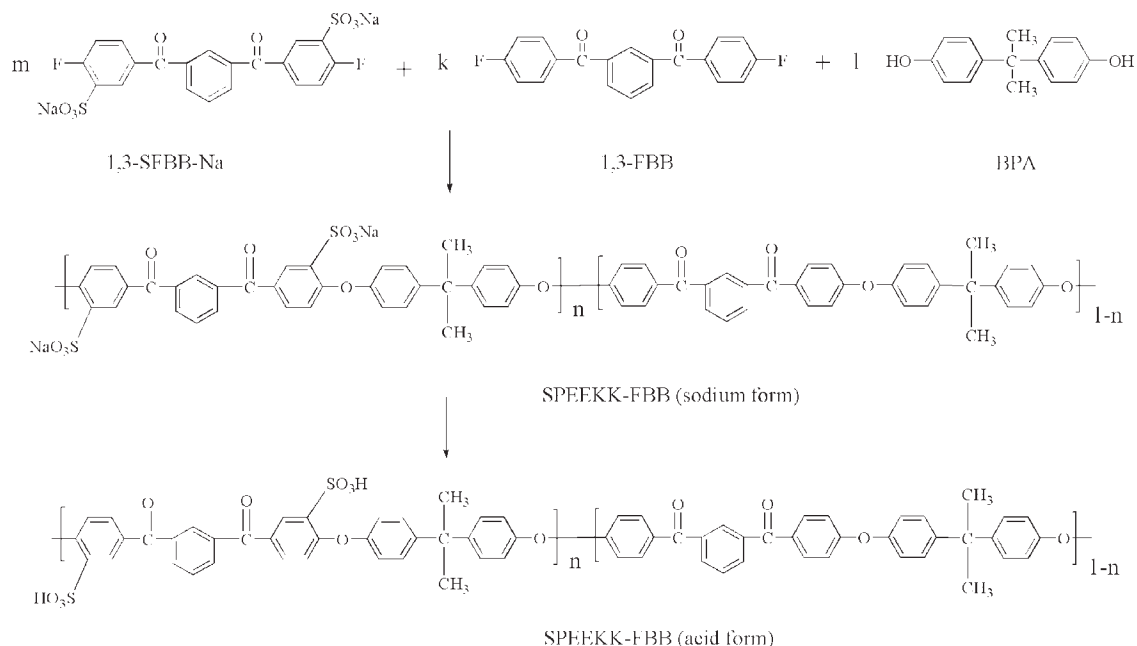
Polymer electrolyte membrane fuel cells (PEMFCs), which typically operated in the temperature range from 60°C to 80°C, have been widely identified for decades as transport, stationary, and portable power source because of their low emissions and high conversion efficiency.<sup>1–5</sup> The polymer electrolyte membranes (PEMs), a solid electrolyte in PEMFCs, were considered as the heart of the PEMFCs, afforded ionic pathways for transferring protons as well as a separator between the electrodes for the reactant gases, proton, fuel and electrons. There is much investigation about the PEMs because of their important role played in successful PEMFCs fabrications.<sup>6</sup> Currently, Nafion<sup>®</sup> (DuPont) widely used in PEMs, represents the current state-of-the-art PEMs because of their good mechanical, thermal, and chemical stability along with good conductivity at moderate temperatures (<90°C). However, high cost, high methanol permeability, low humidity, and a

major reduction in conductivity at high temperatures have limited Nafion's further application.<sup>7–10</sup>

One of the important challenges in fuel cells research area, right now, is to develop alternative membranes with low cost, high proton conductivity. Sulfonated aromatic polymers, such as poly(ether ether ketone)s (SPEEKs),<sup>11–15</sup> poly(ether sulfone)s,<sup>16,17</sup> poly(arylene ether)s,<sup>18–20</sup> polyimide,<sup>21–23</sup> and poly(*p*-phenylene)s<sup>24,25</sup> are widely investigated as candidate PEMs materials. Poly(aryl ether ketone)s were well known for their excellent mechanical properties, high thermal stability, as well as resistance to oxidation.<sup>26–28</sup> In our previous work, we have explored SPEEK membranes for PEMs.<sup>29</sup> These membranes showed better thermal stabilities and methanol resistance compared with Nafion. But the proton conductivity was relatively lower than that of Nafion. It is well known that the PEMs materials usually contained two domain regions: hydrophilic and hydrophobic ones. The hydrophobic domains formed by nonsulfonated polymer segment provide the hydrated PEMs with mechanical strength, whereas the hydrophilic domains contain sulfonated groups ensure the proton conductivity. The existence of the two regions may lead to the microphase-separated structures, which will determine the properties of PEMs such as water swelling, methanol cross over, and proton conductivity and so on.

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**Scheme 1** Synthesis of sulfonated poly(ether ether ketone ketone)s (SPEEKKs).

In this article, we prepared a new sulfonated monomer with metagroup in the structure in which the distance between sulfonated groups was lower than the sulfonated monomer that had been done previously.<sup>29</sup> A series of SPEEKK with different degrees of sulfonation (DS) were prepared by direct synthesis of sulfonated monomer method. The method has been proven more advantageous than that of postsulfonation. Some of the advantages are listed below:<sup>1</sup> Compared with the postsulfonated PEEK, the concentration as well as the positions of the sulfonated groups (e.g., meta, para, and ortho) within the directly synthesized SPEEK can be readily controlled. This allows one to control the DS easily.<sup>2</sup> The direct-sulfonation method avoids the crosslinking and other side reactions, which may result in better thermal stabilities and mechanical properties. The structures of SPEEKKs were characterized by FTIR and <sup>1</sup>H-NMR. The DS of SPEEKKs were obtained by <sup>1</sup>H-NMR. The properties of SPEEKK membranes were investigated in detail. The purpose of this article is to explore excellent membranes for fuel cells usages.

## EXPERIMENTAL

### Materials

1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB) was purchased from Aldrich, 50% fuming sulfuric acid was obtained from Beijing Chemical Work, China. And other reagents were obtained as received and used without further purification.

### Synthesis of 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (1,3-SFBB-Na)

A mixture of 1,3-FBB (32.2 g 0.1 mol) and 50% fuming sulfuric acid (50 mL) was heated at 110°C for 6 h. The solution was then cooled and poured into ice water. The sulfonated compound was neutralized with NaOH and precipitated with NaCl. The crude product was recrystallized with the mixture of methanol and water.

### Synthesis of sulfonated poly(ether ether ketone ketone)s

The synthesis route of the SPEEKKs is shown in Scheme 1. In a 250 mL three-necked round flask equipped with a Dean-Stark trap, a reflux condenser, a nitrogen inlet, and a thermometer, 1,3-FBB (k mol) 1,3-SFBB-Na (mmol), bisphenol A (l mol), dihydrous potassium carbonate, and DMSO were added. In this system, the content of monomer l was kept at 40 mmol, which was equal to the amount of monomer m and monomer k. The DS was controlled by adjusting the ratio of monomer m to monomer k. The temperature of the system was maintained at 140°C for 4 h to remove all the water azeotropically with toluene from reaction mixture and then raised to 180°C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed by washing in boiling water several times. Then the product was dried to get the pure polymers.

### The DS of the SPEEKs polymers

$^1\text{H-NMR}$  was used to identify the molecular structure of the SPEEK polymers and to evaluate the DS. The DS can be derived from the ratio between the peak area of the  $\text{H}^1$  signal and the integrated peak area of the signals of other hydrogen.<sup>30</sup> The DS (mol % of sulfonated units) was determined by the integration of these peaks and with the following equation:

$$\frac{\text{Ds}}{10 - 2\text{Ds}} = \frac{\text{AH1}}{\sum_{\text{Another}} H} \quad (1)$$

### Membrane preparation and characterization

#### Membrane preparation

The SPEEKs were first dissolved in DMF to form 5–10% solutions at room temperature, the resulting solutions were then cast onto glass plates and dried at 85°C for 10 h then in a vacuum oven at 100°C for 48 h. The membranes were removed from the glass plate and were then acidified in 1.0M HCl solutions overnight, and then rinsed with deionized water to remove any excess acid. The membranes in acid form had been obtained.

#### Characterization and thermal properties of SPEEKs

The composition and structure of the polymers in the sodium salt form were confirmed by FTIR and  $^1\text{H-NMR}$ . FTIR measurements were performed with a Nicolet Impact410 FTIR spectrometer. The  $^1\text{H-NMR}$  spectra were measured on BRUKER AVANCZ 500 spectrometer at 298 K with deuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ ) as the solvent and tetramethylsilane (TMS) as the standard. The reduced viscosities of the polymers were measured at 5.00 g  $\text{L}^{-1}$  in DMF at 25°C ( $\pm 1$ ) using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821e instrument at a heating rate of 10°C  $\text{min}^{-1}$  under  $\text{N}_2$  flow. A Pyris-1 (Perkin Elmer) thermogravimetric analysis (TGA) was employed to study the thermal stabilities of SPEEK samples. Before testing, all the polymers were preheated at 150°C for 20 min to remove any residual moisture and solvent. After that, the samples were cooled to 100°C and then reheated to 650°C with a heating rate of 10°C  $\text{min}^{-1}$  in  $\text{N}_2$  flow.

#### Water uptake and swelling ratio measurement

Measurement of water uptake (WU) and swelling ratio was determined from the difference in weight and length between the dried and the swollen membranes. The membranes in acid form were vacuum

dried at 120°C until the constant weights and lengths were obtained. The dried membrane was weighed and then soaked in deionized water for 24 h from 25°C to 80°C until the weight remained constant. It was then taken out, wiped with blotting paper rapidly and weighted. Water uptake (WU) of the membrane was calculated by the following equation:

$$\text{Water uptake (WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weight of water swollen and corresponding dry membranes, respectively.

the swelling ratio was calculated by the following equation:

$$\text{Swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

Where  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the length of water swollen and corresponding dry membranes, respectively.

#### Water retention and water diffusion coefficients

During the process of measurement, TGA was used to determine the weight changes of the membranes with time. The temperature was kept at 80°C for 60 min, and the pressure of the test cell was kept constant. Water diffusion coefficient was calculated as follows:

$$\frac{M_t}{M_\infty} = 4 \left( \frac{Dt}{\pi l^2} \right)^{1/2} \quad (4)$$

where  $Dt$  is water diffusion coefficient,  $M_t/M_\infty$  is the water desorption,  $l$  is the membrane thickness.

#### Ion-exchange capacity (IEC), proton conductivity and methanol diffusion coefficient

The membranes in  $\text{H}^+$  form were immersed in 1M NaCl solutions for 24 h to liberate the  $\text{H}^+$  ions (the  $\text{H}^+$  ions in the membrane were replaced by  $\text{Na}^+$  ions). The  $\text{H}^+$  ions in solution were then titrated with 0.01M NaOH. The IEC were then calculated from the titration date by the following equation:

$$\text{IEC} = \frac{\text{consumed ml NaOH} \times \text{molarity NaOH}}{\text{weight of dried membrane}} \times (\text{mequiv.g}^{-1}) \quad (5)$$

The theoretical IEC calculated from DS was obtained from equation below:

$$\text{IEC} = \frac{1000\text{Ds}}{510 + 80\text{Ds}} \quad (6)$$

The measurements of proton conductivity of the membranes were carried out via the AC impedance spectroscopy using a Princeton Applied Research Model 273A potentiostat with a Model 5210 Frequency Response Detector (EG&G PARC, Princeton, NJ) from 100 mHz to 100 KHz. During testing, the relative humidity was kept at 100% (100%RH), the proton conductivity was calculated by the equation below:

$$\sigma = L/RA \quad (7)$$

Where  $\sigma$  is proton conductivity,  $L$  is membrane thickness,  $R$  is membrane resistance, and  $A$  is membrane area.

Methanol diffusion coefficients of membranes were measured by using a two-chamber liquid permeability cell described in the literature.<sup>13,31,32</sup> This cell consisted of two reservoirs, which were separated by a vertical membrane immersed in deionized water for 24 h. 10M methanol solution was placed on one side of the cell and water was placed on the other side. The magnetic stirrers were used continuously during the measurement. Methanol concentrations in the water cell were periodically determined by using a GC-8A gas chromatograph (SHIMADZU, Tokyo, Japan). The methanol diffusion coefficient was calculated by equation:

$$C_B(t) = \frac{A DK}{V_B L} C_A(t - t_0) \quad (8)$$

where  $A$ ,  $L$ , and  $V_B$  were the effective area, the thickness of membrane and the volume of permeated reservoirs, respectively.  $C_A$  and  $C_B$  were the methanol concentration in methanol chamber and in water chamber, respectively.  $DK$  was the methanol diffusion coefficient.

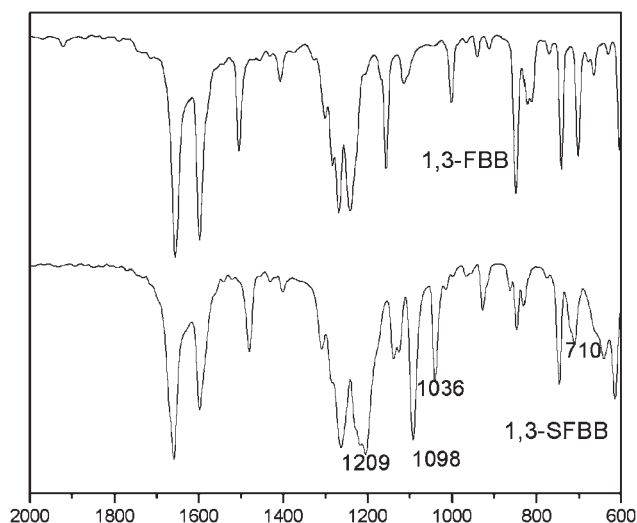
### Mechanical properties

The tensile strength of the membranes was measured using SHIMADZU AG-I 1KN at a test speed of 2mm min<sup>-1</sup>, and the size of specimen was 15 mm × 4 mm. For each testing reported, at least three measurements were taken and an average value was calculated.

## RESULTS AND DISCUSSION

### Synthesis of monomer

A new sulfonated monomer 1,3-SFBB-Na was prepared by sulfonation of 1,3-FBB with fuming sulfuric acid. On the basis of the electronic theory of orientation in electrophilic aromatic substitution, the principal sulfonation, the location of sodium sulfonated



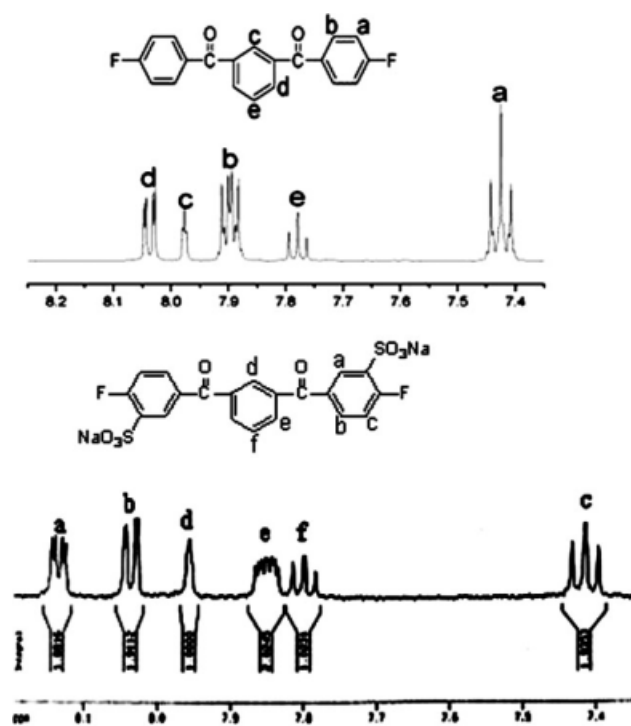
**Figure 1** The FTIR of the sulfonated monomer and non-sulfonated monomer.

groups is meta to the carbonyl group and ortho to the fluorine group. The chemical structure of the monomer was assigned on the basis of FTIR (Fig. 1), elemental analysis, <sup>1</sup>H-NMR (Fig. 2), and Mass Spectrometry. From the FTIR in Figure 1, the peaks at 1209, 1036, and 1098 cm<sup>-1</sup> are assigned to the characteristic vibration of sulfonated groups. Compared with the sulfonated monomer, there were not related vibrations in nonsulfonated monomer. The <sup>1</sup>H-NMR of sulfonated monomer and nonsulfonated monomer in Figure 2 has indicated the corresponding peaks. Due to the introduction of sulfonated groups, the H atom beside the sulfonated groups shifted to the higher ppm compared with nonsulfonated monomer. The element analysis of the sulfonated monomer was well confirmed to the calculated values, which confirmed the sulfonated monomer had been synthesized successfully.

### Preparation and characterization of the polymers

As shown in Scheme 1, the SPEEKs were prepared by the aromatic nucleophilic substitution polycondensation of bisphenol A with different ratio of 1,3-SFBB-Na (monomer m) to 1,3-FBB (monomer k) in a DMSO/toluene solvent system. The polymerization results and analytical data are displayed in Table I. The specific viscosity indicated that all the polymers had high molecular weights. It was interesting to find out that the specific viscosity of SPEEK shows increased tendency with the increasing content of sulfonated groups. This may be explained by the factors that influenced this reaction, a classical nucleophilic aromatic substitution. In this reaction, the initial step involves the attack of the nucleophile at the activated site to form a resonance stabilized arenium ion intermediate, which is generally accepted to be

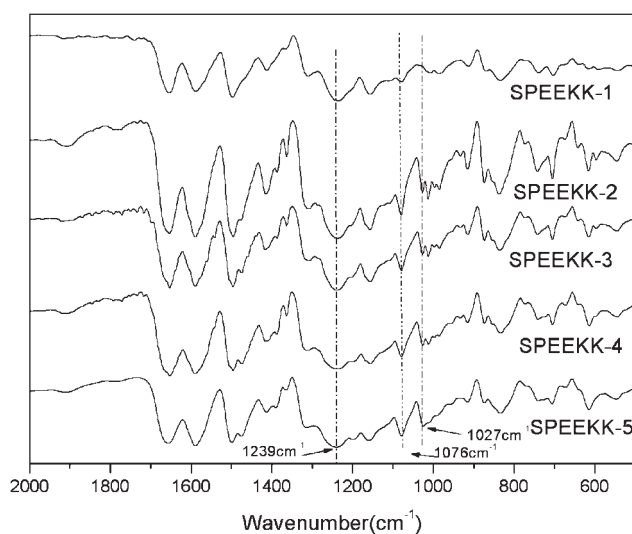




**Figure 2** The  $^1\text{H-NMR}$  of the sulfonated monomer and nonsulfonated monomer.

the rate determining step. The introduction of sodium groups may lead to the following results: the electron withdrawing property of sodium groups will decreasing density of electron cloud of the activated site in this reaction, which may increase the activity of this reaction. However the steric hindrance of it will decrease the activity. The former factor plays the determined role in this system so the specific viscosity of SPEEKs increased with the increasing content of sulfonated groups.

Figure 3 shows the FTIR spectra of polymers. The absorption bands at  $1027\text{ cm}^{-1}$  were assigned to the S=O stretching of the sodium sulfonated groups. The absorption bands at  $1076\text{ cm}^{-1}$ ,  $1239\text{ cm}^{-1}$  were assigned to asymmetric and symmetric O=S=O stretching vibrations of the sodium sulfonated



**Figure 3** The FTIR spectra of SPEEKK polymers.

groups. No peaks attributed to the aromatic sulfonated group in the range of  $1140\text{--}1110\text{ cm}^{-1}$  were found, which indicated that no cross linking occurred during copolymerization.

$^1\text{H-NMR}$  spectra provided unambiguous structure elucidation. Figure 4 shows the aromatic region of a  $^1\text{H-NMR}$  spectrum of SPEEKK-5 polymer sample. Each signal was assigned to a single or to a group of aromatic protons. The different feed ratios of sulfonated monomer added complexity to the spectra. Therefore, we did not attempt to assign all the signals from the SPEEKK copolymers.

Table I shows that the DS calculated from  $^1\text{H-NMR}$  were well consistent with values got from calculation, which clearly suggested that DS could be readily manipulated by controlling the amount of sulfonated monomer added.

### Thermal properties and solubilities of polymers

Table I also lists the  $T_g$  of SPEEKK-1, SPEEKK-2, and SPEEKK-3 in acid salt form, which showed  $T_g$  increased with DS increasing from  $151.2$  to  $157.3^\circ\text{C}$ .

**TABLE I**  
The Data of the Sulfonated Polymers

Polymer	m (mmol) <sup>a</sup>	k (mmol) <sup>a</sup>	m/k	Yield (%)	$\eta_{sp}/c^b$	$T_g$ ( $^\circ\text{C}$ )	$T_{d10\%}$ ( $^\circ\text{C}$ ) <sup>c</sup>	DS (cal) <sup>d</sup>	DS (meq) <sup>e</sup>	DS (nmr) <sup>f</sup>
SPEEKK-1	4	36	1 : 9	93	0.44	151.2	526.3	0.2	0.16	0.2
SPEEKK-2	8	32	2 : 8	94	0.52	156.8	459.9	0.4	0.36	0.39
SPEEKK-3	12	28	3 : 7	93	0.58	157.3	432.3	0.6	0.50	0.58
SPEEKK-4	16	24	4 : 6	90	0.63	–	382.9	0.8	0.66	0.79
SPEEKK-5	20	20	5 : 5	92	0.60	–	346.3	1.0	0.79	1.02

<sup>a</sup> The content of monomer m and monomer k in the reaction.

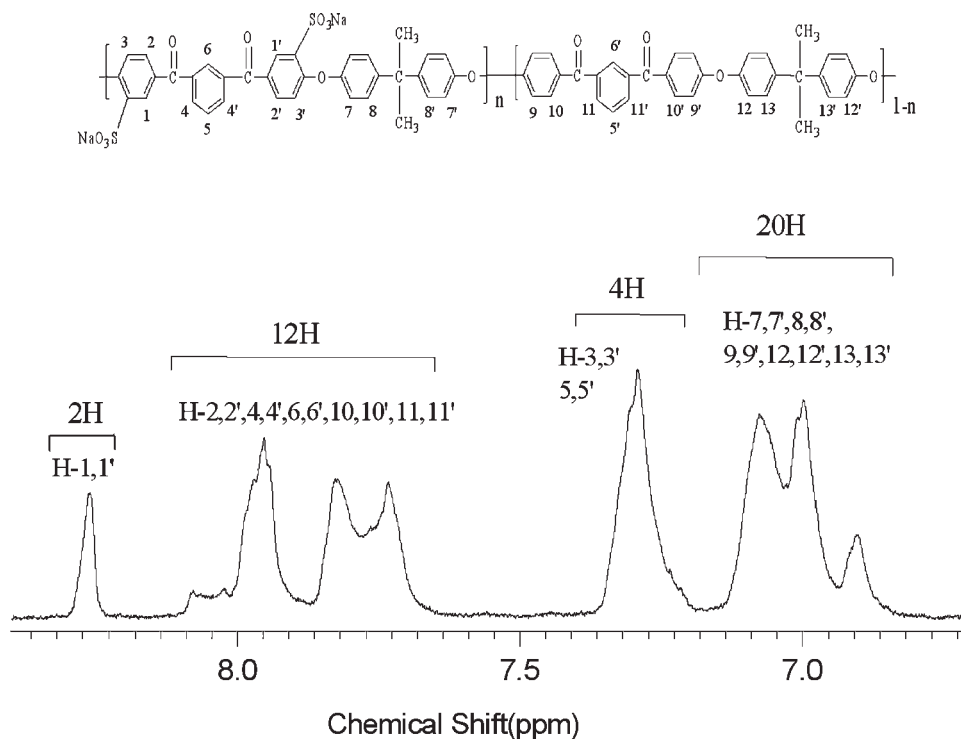
<sup>b</sup> Measurement of reduced viscosity at a concentration of  $5.00\text{ g/L}$  in DMF at  $25 + 0.1^\circ\text{C}$ .

<sup>c</sup>  $T_{d10\%}$ : The temperatures for 10% weight loss.

<sup>d</sup> Degrees of sulfonation (DS) obtained by calculation.

<sup>e</sup> Degrees of sulfonation (DS) obtained by titration.

<sup>f</sup> Degrees of sulfonation (DS) obtained by NMR.

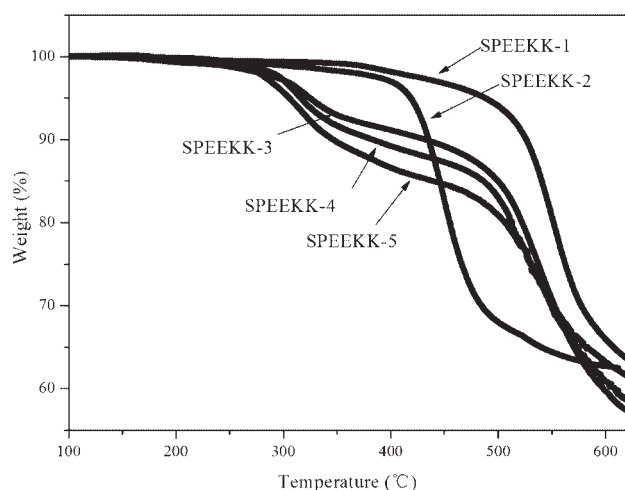


**Figure 4**  $^1\text{H-NMR}$  spectra of SPEEKK-5 (Ds 0.79).

This may be due to the introduction of sulfonic acid groups that increased intermolecular interaction by pendant ions or by hydrogen bonding and molecular bulkiness and hinder the internal rotation of high molecular chain segments. The TGA curves of the SPEEKK polymers in acid form are showed in Figure 5. In similarity with observations previously, there are two distinct weight loss steps in the TGA curves of SPEEKK polymers.<sup>13,16,17</sup> Figure 5 shows that the extrapolated onset temperatures are higher than  $300^\circ\text{C}$ , indicating the high thermal stabilities of acid form SPEEKK polymers at high temperatures. Table I shows that  $T_{d10\%}$  decreased with an increase

of the sulfonated groups in the polymer chain. This may be due to the thermal decomposition temperature of the sulfuric acid groups was lower than that of the backbone of the polymers.<sup>26</sup> The second thermal degradation around  $450^\circ\text{C}$  is assigned to the degradation of the polymer main chain.

All the resulted polymers show excellent solubility in aprotic dipolar solvents such as DMF, DMSO and NMP. SPEEKK-4 and SPEEKK-5 were swollen in water at high temperatures and SPEEKK-1, SPEEKK-2, and SPEEKK-3 were insoluble in water. This can be explained by the increased solubility between polymers and water because of the increasing content of sulfonated groups in polymer backbone.

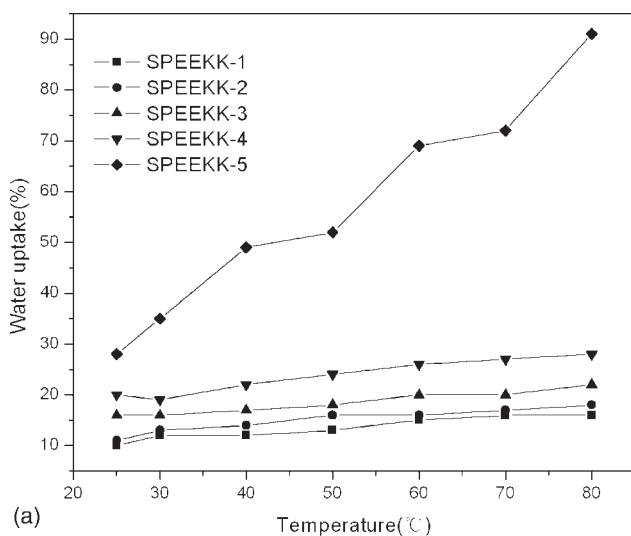


**Figure 5** TGA curves of SPEEKK polymers in acid form.

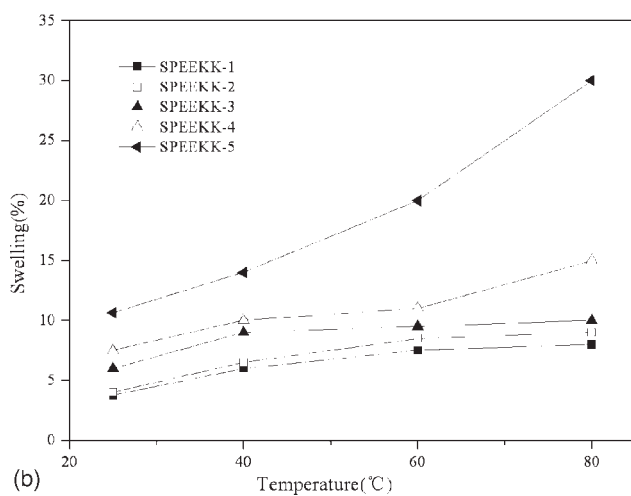
### The properties of membrane

#### Water uptake, swelling ratio, and water desorption

Water uptake and swelling of membranes are two factors that influence the properties of PEMs. First, the water content of membranes largely influenced proton transport in SPEEKK membranes. The proton conductivities increased when water uptake increased, because the proton exchange reactions required a significant amount of water to coordinate with proton as it moved through the membrane. Ionic membranes did behave like insulator in dry state but become conductive when hydrated. Second, the water uptake would influence the mechanical properties very much, when the PEMs were using in



(a)



(b)

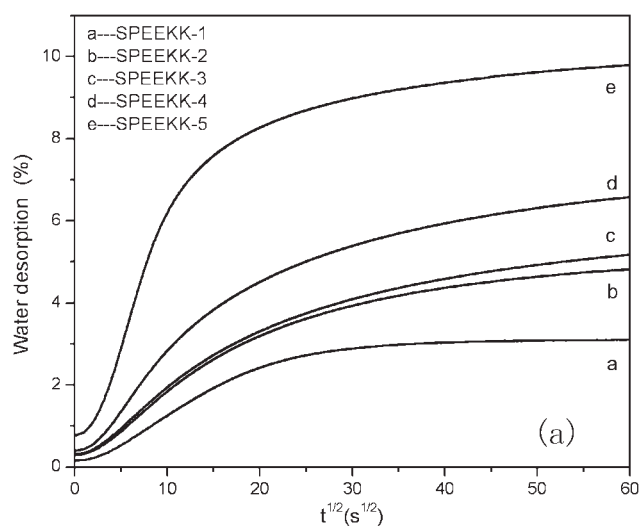
**Figure 6** Water adsorption properties of SPEEKK membranes as functions of temperature. (a) water uptake and (b) water swelling.

the real fuel cells environment. So the select membranes with appropriate levels of water uptake were very important. It has been reported that in the presence of water the sulfonic polymers exhibit hydrophobic/hydrophilic nanophase separation, whereby the sulfonic acid groups form hydrophilic hydrated domains contributing to the proton conductivity and the nonsulfonated backbone forms a well-networked hydrophobic domain providing mechanical strength.<sup>13,33</sup> Figure 6 and Table II display water uptake (wt %) and linear swelling (%) of SPEEKK membranes in the acid form at different temperatures. The swelling and water uptake were determined as functions of temperature. Figure 6(a) clearly shows that the water uptake continued to increase with DS and temperatures and particularly sharply increased for SPEEKK-5. All the water uptakes were lower than that of Nation 117, which may be the influence of the position of sulfonated

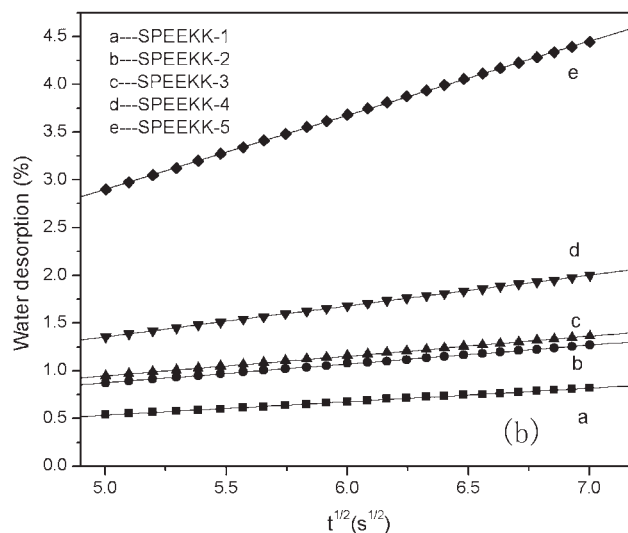
**TABLE II**  
Water Uptake, Swelling Ratio, and Water Desorption of SPEEKK Membranes at Different Temperatures

Polymer	Water uptake (%)		Swelling ratio (%)		Water diffusion coefficient (cm <sup>2</sup> /s)
	25°C	80°C	25°C	80°C	
SPEEKK-1	10	15	4	8	$2.987 \times 10^{-9}$
SPEEKK-2	12	18	4	9	$8.870 \times 10^{-9}$
SPEEKK-3	16	23	6	10	$1.764 \times 10^{-8}$
SPEEKK-4	20	28	7	15	$4.685 \times 10^{-8}$
SPEEKK-5	28	91	11	30	$9.334 \times 10^{-8}$
Nafion-117	19	30	13	20	–

groups in polymers on the microstructure of SPEEKK membranes. Therefore, only the hydrophilic domain of the nanostructure was hydrated in the presence of water. The sulfonated groups in SPEEKKS dispersed through aromatic matrix, which is less hydrophilic than Nafion. All these



(a)



(b)

**Figure 7** The water desorption isotherm of SPEEKK membranes, (a) curvic isotherm and (b) linear isotherm.

**TABLE III**  
The Properties of Membranes in Acidic Form

Polymer	d <sup>a</sup> (μm)	IEC(mmol/g)		Methanol diffusion (cm <sup>2</sup> /s)	Proton conductivity (S/cm)	
		Calculated	Measured		25°C	80°C
SPEEKK-1	45	0.38	0.18	$4.29 \times 10^{-8}$	0.005	0.012
SPEEKK-2	41	0.73	0.53	$9.36 \times 10^{-8}$	0.014	0.026
SPEEKK-3	52	1.07	0.82	$1.56 \times 10^{-7}$	0.028	0.040
SPEEKK-4	33	1.39	0.97	$2.86 \times 10^{-7}$	0.037	0.056
SPEEKK-5	45	1.69	1.40	$5.03 \times 10^{-7}$	0.052	0.075
Nafion-117	175		0.92	$2 \times 10^{-6}$	0.080	0.10

<sup>a</sup> Thickness of membranes.

characteristics of SPEEKK membranes may lead to the lower water uptake than Nafion. Figure 6(b) shows the linear swelling of SPEEKK membranes at different temperature. The results show that the linear swelling increased with the increment of DS. The linear swelling of different membranes increased with the range from 8 to 30% at 80°C.

It is one of the drawbacks that Nafion has low water retention at high temperatures, which baffled their further commercial application. Water retention in this work was analyzed by the velocity of water evaporation of the membranes.<sup>34</sup> Water desorption isotherm curves of SPEEKK membranes are shown in Figure 7. It shows that water loss increased gradually from SPEEKK-1 membrane to SPEEKK-5 membrane. The relationships between the water desorption and time might follow Ficker diffusion. Plots of  $M_t/M_\infty$  versus  $t^{1/2}$  initially were linear for Ficker's diffusion, which is shown in Figure 7(b). Diffusion coefficients for water desorption were calculated from the initial slopes of the line according to equation (4). Table II showed that the water diffusions of SPEEKK-1 to SPEEKK-5 membranes were  $2.987 \times 10^{-9}$ ,  $8.870 \times 10^{-9}$ ,  $1.764 \times 10^{-8}$ ,  $4.685 \times 10^{-8}$ , and  $9.334 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ , respectively. The water diffusion coefficient of the SPEEKK membranes increases with the increment of DS.

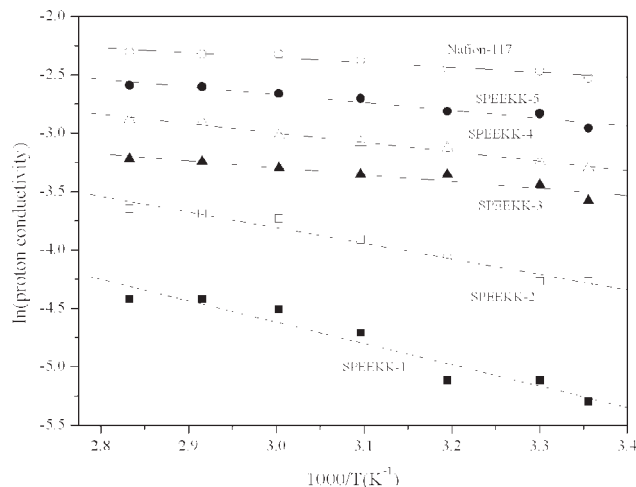
#### Ion-exchange capacity, proton conductivity, and methanol diffusion coefficient

IEC values of the membranes were well controlled during synthesis by varying sulfonated monomers feed ratio. The IEC was determined by both of titration and calculation method. Table III shows that the two IEC values are in good agreement with each other, and both of them increased with the DS. The IEC play a critical role in determining the proton conductivity of membranes.

Proton conductivities of the membranes at different temperatures were calculated from resistance measurement. The conductivity data was analyzed in terms of Arrhenius plot, as reported in Figure 8.

The proton conductivities at different temperatures are shown in Table III. It can be seen that proton conductivities increased when DS (or IEC) and temperature increased. Compared with Nafion, SPEEKK membranes showed relatively lower proton conductivity, which was due to the different distribution of ion domains in membrane.<sup>1</sup> This is attributed to the lower hydrophobicity of SPEEKK polymer backbone compared with the perfluorinated backbone of Nafion, as well as a relatively strong interactions between the water molecules and sulfonic acid groups,<sup>4</sup> which would result in improved water retention and high proton conductivity at elevated temperature. Nafion with more ion-rich domains allowed the ions to move more easily than SPEEKK. SPEEKK-4 and SPEEKK-5 show similar proton conductivity at 80°C with Nafion, which may be an indication that percolation in the hydrophilic domain of these two polymers is possibly similar to that of Nafion 117.<sup>33</sup>

Table III shows that SPEEKK membranes exhibited increasing methanol diffusion coefficient from  $4.29 \times 10^{-8}$  to  $5.03 \times 10^{-7} \text{ cm}^2/\text{s}$  at 25°C. The results suggested the influence of the sulfonated group



**Figure 8** The proton conductivities of membranes compared with Nafion 117 at different temperatures.



**TABLE IV**  
**The Mechanical Properties of SPEEKK Membranes**

Polymer	Tensile modulus Gpa	Maximum elongation %	Tensile strength Mpa
SPEEKK-1	1.69	10.01	54.85
SPEEKK-2	1.52	9.57	50.70
SPEEKK-3	1.31	11.86	50.19
SPEEKK-4	1.30	8.67	48.23
SPEEKK-5	1.27	7.40	46.87

position on the hydrodynamic solvent transport (water and methanol) properties of membranes. In the SPEEKK membranes sulfonated groups dispersed throughout the polymer matrix and were not easy to lead a phase separation, meanwhile in Nafion the sulfonated groups were on the side chains of the polymers and may easily lead to a phase separation.<sup>35</sup> All these characteristics will lead to the methanol diffusion coefficient of the SPEEKK membranes much lower than that of Nafion ( $2 \times 10^{-6} \text{cm}^2/\text{s}$ ).

#### Mechanical properties of SPEEKK membranes

Table IV shows the mechanical properties of SPEEKK membranes. The SPEEKK membranes showed relatively better mechanical stability than Nafion at ambient condition. The initial Young's modulus for the SPEEKK membranes is 1.69, 1.52, 1.31, 1.30, and 1.27GPa, respectively, which are higher than that of Nafion 117 (0.25 MPa). The maximum elongations of all the SPEEKK membranes were in the range of 7.40 to 11.86%, and tensile strength ranging from 47 to 55 MPa. All the results indicated that the SPEEKK membranes were strong and tough enough for use in PEMFC.

#### CONCLUSIONS

SPEEKK with different DS were prepared by directly polymerization of sulfonated monomers. DS of the SPEEKKs were determined by <sup>1</sup>H-NMR spectroscopy. All the polymers were easily cast into tough membranes. SPEEKK membranes showed good proton conductivities and excellent thermal stabilities. The proton conductivity of SPEEKK-5 is 0.052 S/cm at room temperature and 0.075 S/cm at 80°C. Also, the membranes showed much better methanol resistance than Nafion. The methanol diffusion is at the range of  $4.29 \times 10^{-8}$ – $5.03 \times 10^{-7} \text{cm}^2/\text{s}$ , which is much lower than Nafion ( $2 \times 10^{-6} \text{cm}^2/\text{s}$ ) at the same temperature. The membranes also showed better mechanical properties than Nafion. All the results showed that the SPEEKK polymer is one kind of potential candidate for PEMFC usage.

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